Observation of microphase segregation in binary polymer brushes

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INTRODUCTION

The basic idea is creation of smart polymer layers with switching properties such as wetting behavior, adhesion, interaction with biological objects, and permeability of membranes. Such polymer layers can find their application in many areas such as information recording, sensors, self-cleaning clothes covering, nanodevices, in medicine and biological science for mimicking living cell membranes, for selective adsorption and recognition of proteins and living cells. The route, how to make this dream true, comprises binding to solid substrate different polymers[1] or block-copolymers and switch the film structure in such a way, that this film responding to various external stimuli can adopt particular desired properties: hydrophylic/hydrophobic balance, selective adsorption of particular molecules, etc.

We are currently studying model layers composed of two different (hydrophilic and hydrophobic) linear polymers covalently grafted to silicon substrates which can be switched upon exposure to solvents of different thermodynamical quality[1]. The grafting density is so high that the distance between grafting points of neighbor polymer molecules is much (about 10 times) shorter than the size of the polymer coils (mean distance between chain ends in theta-conditions). Therefore the polymer coils interact with their neighbors and are elongated in the direction perpendicular to the substrate. All the conformational changes are cooperative. Such regime is known as the brush regime. If such a binary polymer brush is exposed to a selective solvent which good for the first brush polymer and poor for the second one the first polymer swells and occupies the top layer while the second polymer collapses and occupies the bottom layer near the substrate. If the solvent is replaced by another one with opposite selectivity the brush passes to a state inverse with respect to the previous one. In a solvent good for both polymers they both are present on the top of the layer. The time of solvent evaporation upon drying by nitrogen flow is much smaller than the time for morphology transformation. The morphologies after treatment in a particular solvent are reproducible and reversibly switch upon changing the solvent. We made the assumption that the spacial distribution of the polymers in the dry state after exposition to a solvent is a fingerprint of their distribution under the solvent[2].

The polymers are usually incompatible but only microphase segregation takes place because each polymer chain is chemically bound to a substrate with one end. The size of the aggregates is limited by the chains` length. Two limiting types of morphologies can be distinguished: the layered phase with only perpendicular phase segregation and the “ripple” phase with lateral segregation. Analytical studies of the microphase segregation in binary brushes under melt conditions and in various solvent conditions were done. Self consistent field calculations made by Marcus Müller[2] predict for binary polymer brushes in a solvent good for both components existence of the “ripple” phase consisting of parallel lying cylinders with alternating enrichment by each brush component. For the case of a selective solvent an existence of the “dimple” phase is predicted where the worse soluble polymer forms round clusters and the other polymer occupies the area around them. Experimental observation of microphase segregation in binary polymer brushes was performed using facilities of the Ernest Orlando Lawrence Berkeley National Laboratory and was briefly reported elsewhere[2].

RESULTS

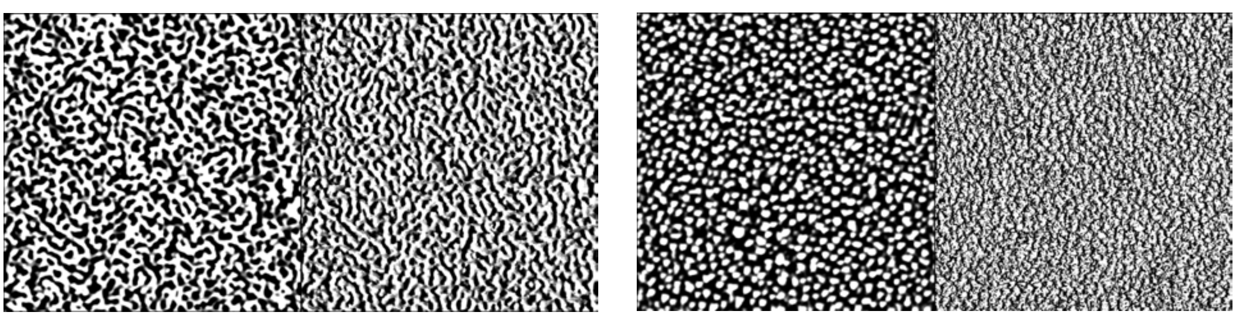
We synthesized binary polymer brushes by radical polymerization on a Si surface using for the grafting of the second polymer the residual azo-initiator on the surface[1]. The brush components were polystyrene with 25% of fully fluorinated aromatic rings (P(S-co-FS)) and polymethylmethacrylate (PMMA).

We observed the reversible morphology switching from elongated species after treatment in toluene to round clusters after exposition to acetone with Atomic Force Microscopy (AFM) (see Fig.1).

We investigated the chemical composition of the brushes` top layers (≤5 nm) after exposition to toluene and acetone applying X-Ray Photoelectron Emission Microscopy (XPEEM). The difference between the carbon peaks in Near Edge X-Ray Absorption Fine Structure spectra (NEXAFS) for polystyrene (286.1 eV) and PMMA (289.3 eV)[3] was used to distinguish between the polymers. We observed the inverse contrast of elongated species at the XPEEM images recorded at 286.1 eV and 289.3 eV for the brush exposed to toluene (see Fig.2). We were unable to find any chemical contrast at the XPEEM images for the brush exposed to acetone due to a strong signal distortion caused by highly rough brush surface.

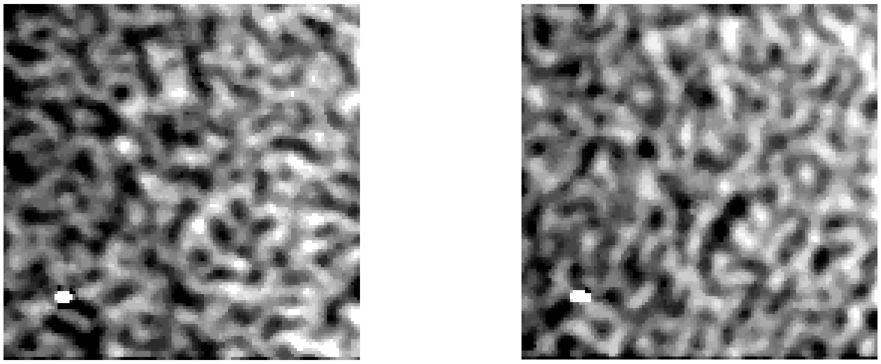
The integral NEXAFS spectra were recorded from the surfaces of the brushes after exposure to toluene, acetone, and after annealing at 150ºC for 24 hours in vacuum. The water contact angle on the same surfaces was measured. The chemical composition of the top layers of the brushes was calculated and similar results were obtained from these two methods. The top layer of the brushes was enriched with P(S-co-FS) after exposition to toluene and after annealing and with PMMA after exposition to acetone (see Table 1).

We conclude qualitative agreement of the experimentally observed morphologies with the self consistent field calculations.



A B C D

Figure 1. AFM tapping mode images 5x5 μm of the P(S-co-FS)/PMMA brush after exposure to toluene (A,B) and acetone (C,D): topography (A,C), phase (B,D) at 50% set-point ratio.



A B

Figure 2. XPEEM images 3x3 μm of the PSF-PMMA1 brush after exposure to toluene showing contrast between C edges of both polymers at 286,1 eV (A) and 289,2 eV (B) for PS and PMMA, respectively.

Table 1. Fraction of PMMA in the top layer of the brushes after exposure to solvents and annealing.

Sample	Contact angle, deg	PMMA fraction in the top layer, % calculated from the contact angle	PMMA fraction in the top layer, % calculated from the XPEEM data
P(S-co-FS)	96.6	0	0
PMMA	76.1	100	100
P(S-co-FS)/PMMA brushes after:			
exposure to toluene	90	32	29
exposure to acetone	81	76	78
in vacuum, at 150°C for 10h	91.5	25	20

REFERENCES

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